

Coherent quasielastic neutron scattering and correlations between rotational jumps of molecules on a periodic lattice

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We previously (G. Coddens, Phys. Rev. **63**, 064105 (2001)) derived a theorem about the *coherent* quasielastic neutron-scattering signal from a d -dimensional lattice of N molecules that are undergoing rotational jump diffusion (around an n -fold axis), assuming that there are no correlations between the molecules. In the present paper molecular correlations are treated, but only in the sense that several molecules could reorient simultaneously as in a cog-wheel mechanism. Moreover, we do not examine the possibility that the relaxation times of these combined reorientations could depend on details of the local environment created by the neighbouring molecules. Finally also an ergodicity condition has to be fulfilled. Admitting for all these assumptions we can show that the correlations do not affect the coherent quasielastic scattering pattern in the following sense: The functions of Q that intervene in the description of the intensities remain unaltered, while the functions of ω can undergo a renormalization of the time scales. The latter changes cannot be detected as the time scales that would occur if the dynamics were independent are not available for comparison. In other words: Coherent quasielastic neutron scattering is not able to betray the existence of correlations of the restricted type that occur in our model. The assumptions that underly the model we present were made to allow a mathematically rigorous calculation of the scattering function. Other, perhaps more realistic cases may entail correlations of a type that is too difficult to be treated rigorously with our method of calculation. But our result presents an important non-trivial counterexample to show that the absence of a clue for the presence of correlations in the data is not a sufficient criterium to conclude that such correlations are indeed absent.

61.12.Ex, 87.64.-t, 66.30.Dn

I. INTRODUCTION

In a recent paper [1] we calculated the coherent quasielastic neutron-scattering signal [2–4] that results from n -fold rotational jumps of N molecules periodically arranged on the sites of a d -dimensional solid-state lattice, by applying a previously described method. [5] *The jumping molecules themselves do not need to have n -fold symmetry.* As a physical visualization of the present problem we could mention the array of nonadecane molecules hosted by an urea inclusion compound. [6] (Such molecules have CH_3 end groups of three-fold symmetry, but the entire molecule has no such symmetry).

In a first approach, we assumed that the molecules are jumping independently, leaving open the question: What could happen if the relaxational motions of neighbouring molecules cease to be uncorrelated? We anticipated that in that case coherent quasielastic neutron scattering might be able to evidence possible correlations. In the present paper we address this possibility, understanding the word correlation in the sense that within connected sets of a given size and shape all molecules jump simultaneously in some phase or anti-phase relations, like in a cog-wheel mechanism. In the paper we will use the word “clusters” to refer to these sets. Assuming further that the relaxation times for these combined jumps do not depend on the momentaneous orientations of the molecules inside (and outside) the cluster, we come to the astounding (and disappointing) conclusion that such correlations do not leave a fingerprint in the structure factors of the ensuing coherent dynamical signal. (See the abstract or below for a more precise formulation of the restrictions). In other words: It is impossible to extract information on the presence and/or the nature of such correlations from coherent quasielastic neutron scattering signals alone.

Let us point out where the surprise lies. Quite often, if we calculate the total structure factor for such dynamics within a single isolated cluster, we will be able to detect the presence of such correlations, as we do not find the same answer as for the jump dynamics of a single molecule. Even when the cluster is not isolated, highly correlated rotors still can be expected to manifest themselves very differently in reciprocal space than randomly independent rotors, e.g. in a linear chain anticorrelated *configurations* produced by the dynamics would manifest themselves at the Q -value corresponding to the zone boundary of the reciprocal lattice. Indeed, the correlated dynamics can give rise to static correlations between the orientations of the molecules, that should be observable. How is our result then possible? This question resumes one of the counter-intuitive aspects of our result.

The snag is that the clusters we consider can be centered on any point of the crystal lattice, such that two clusters situated on neighbouring points can overlap. If the cog-wheels of two such points have ground in succession then the rotations involved in the second move will partly undo the static correlations that existed between the molecules after the first move. In such kind of dynamics the correlations are no longer as all-out that we can call them “ferro” or “anti-ferro” (as in the example of anti-correlated configurations above). To complicate things further, they are not necessarily zero either. They can be of an intermediate strength. How the story unwinds further, really will depend on the specific dynamics defined within the cog-wheel mechanism. E.g. it is conceivable that in certain dynamical models the memory of the initial static correlations in a single cluster (or in the crystal), eventually are totally washed out with time, due to the game of overlapping clusters. We then have a different situation than the one evoked for a problem of an isolated cluster where the static correlations might persist indefinitely. Equally conceivable are other models, where such a total loss of memory does not occur.

We will distinguish two mutually exclusive possibilities: (1) The loss of memory with time is total, such that starting from any initial configuration that one could obtain by independent dynamics we can stray to any other configuration that could be obtained by independent dynamics. We will call this the ergodic case. (2) On the contrary, in the non-ergodic case not all configurations can be reached. The configuration space that applied for the independent dynamics then splits up in several disjoint subsets. Only one of these is the set of possible states of the sample under study. All other states just do not exist in the sample.¹

Neutron scattering calculations involve an average over all possible initial states. In the ergodic case, this averaging will run over the same set of initial states as in the case of independent dynamics. In the non-ergodic case, the set is smaller. We are able to prove that this kind of averaging over all possible configurations of the molecules in the ergodic case is able to iron out the signature of a correlation that was present in the dynamics of an isolated cluster in reciprocal space, i.e. we recover the result for a single molecule. In the non-ergodic case, we average over a smaller set of possible states. This kind of weaker averaging does not permit us to assert that we would recover the result for a single molecule. That is the result of our paper.

At this point it is perhaps instrumental to summarize the situation at the hand of an example. Let us take a linear chain whose $2N$ molecules can take only two orientations (which we can call pseudospins). We suppose that the dynamics is given by some rule that two neighbour sites can flip simultaneously their pseudospins (by two-fold rotations). If this rule defines permanent dimers in the sense that only molecules 1+2, 3+4, 5+6, etc. can turn simultaneously, then we are in the presence of a strong correlation. The presence of such dimers is immediately obvious on an instantaneous photograph of the system and will leave an unmistakable fingerprint in the dynamics. That is the case we are all familiar with. And it is on this case that we all built our intuition.

We render the situation far more subtle by allowing the dimers to be dissociated by the game of overlapping clusters.² Let us first consider a simultaneous flip of the molecules on sites 1 and 2 (starting from a completely aligned configuration). That introduces a correlation. Now assume that an analogous flip involving sites 2 and 3 follows. Will this remove the “correlation”, as the “image” of the initial “dimer” has been destroyed? The answer is (here) that some less conspicuous correlation remains. Due to the construction of the model there will always be an even number of flipped pseudospins. How weak it ever might be, this is a (static) correlation that will never disappear from the model. In fact, due to the persistence of these static correlations, the system is not ergodic and does not fulfil the assumptions that are underlying our paper. But in this very specific case it happens that we can actually prove that the model does *not* yield the same neutron answer as a system with totally uncorrelated molecules. One can easily check this by using our method of calculation on a small toy model and exploiting the fact that the configuration space for the uncorrelated case splits into two disjoint subsets when we introduce the dynamical correlations. But if in another type of dynamical model the configuration space were not to split, then we will be able to assert with

¹Classifying the system according to this distinction was not motivated by the physics. This choice mainly reflects the limits of our abilities to perform certain calculations. The distinction we make codes information about what happens to the system at infinite times: The correlations are eventually lost or otherwise. Nothing is stated about correlations that might persist for finite times. Despite this lack of information about the situation at finite times, in case (1) we will be able to infer an impossibility to discern indications for the presence of correlations within the dynamical signal.

²There is then no longer equivalence between the concepts of a dimer and of a (dynamical) cluster as it is used by us in this paper. We use the terminology “dynamical cluster” to indicate the presence of a dynamical correlation, and to define sets of molecules that are supposed to be able to turn together, while the terminology “dimer” indicates the presence of a fixed orientational relationship between two molecules. Our use of the word “cluster” has also nothing to do with the idea of a domain wherein all molecules would have some special orientational relationships, e.g. to be aligned in a parallel fashion as in a ferromagnet. Our definition of the word cluster is a purely mathematical one. It is thus different from the usual intuitive physical idea.

certainty that the dynamical signal will not offer clues as to the presence of the dynamical correlations.

II. MOTIVATION OF THE USE OF OUR METHOD

A many reader might find the mathematical leap we will take to configuration space too cumbersome and too much of a fuss to his taste. Is all this really necessary? Part of the answer may reside in the following warning against a possible confusion. Consider the following (fallacious) argument. When we look at an instantaneous photograph of an ergodic system, the orientations of the molecules will in general look completely random. From this observation it takes only one step to argue that the “correlations are random”. Would that not show that our result is trivial? [7] The problem is that the word “correlation” occurs with several different meanings in this context. The (spatial) *static* correlations between the orientations of the molecules that would be visible in an instantaneous photograph of the sample may well be random.³ However, the instant *dynamical* (or temporal) correlations are not random, as they tie up a well-defined set of molecules into a cog-wheel.

To avoid confusion, it is thus important to realize that the word correlation can intervene with two entirely different meanings in the discussion and in the mind of the reader. We have *static* orientational correlations between the molecules of the whole crystal that we may detect in a snapshot of the system. We call such snapshots configurations. These static correlations are the ones that matter in structural diffraction techniques. One will run headlong into trouble if one does not properly sort out for oneself that moving to a dynamical context involves a shift of paradigm: We have to consider *temporal* correlations between *pairs* of such snapshots at *all* possible times. The cog-wheel mechanism defines *dynamical* correlations between molecules within a (small) cluster, in the sense that it tells you which molecules will turn simultaneously and how they will turn. The dynamical correlations are the ones that really count, not the static ones, although the former are of course responsible for the occurrence of the latter. In view of this remark, the loose phrasing “in the presence of correlations” appears thus as fraught with ambiguity.⁴

An important aspect of our method is that it develops a precise mathematical tool that permits to discuss all kinds of details that can arise in an argument about correlations in a very clear and rigorous way, without running into difficulties due to certain inadequacies of plain language. The examples of the correlations that persist on a linear chain despite the dissociation of the dimers and of the fallacy based on the ambiguous use of the phrasing “random correlation” as sketched above may serve to show how heedless it is to underestimate the difficulty of deciding on one’s mere intuition if a correlation is present within a system or otherwise, and how discussing such matters in informal language can seed confusion. Two persons may easily use the same words and sentences to refer to mental pictures in their heads that are fundamentally different, without being aware of these differences. In a casual discussion it might e.g. take quite some time before it transpires that a person does not take properly into account the vital distinction between static and dynamical correlations we outlined above. The reverse of the medal is that mathematical rigor all too often leads to austere if not frustrated reading.

III. POSSIBLE DOMAINS OF APPLICATION OF THIS WORK

A. Scope of experimental probes

We are presenting our work in terms of a coherent neutron scattering problem, but the formalism will also apply to other microscopic techniques, provided the scattering is really coherent and the technique allows to obtain a Q -dependence. Coherent scattering does not only occur with neutrons when the nuclei have an important coherent scattering cross-section. In contrast with neutron scattering, where the nuclei can have both a coherent and an incoherent scattering cross section, X-ray and light scattering processes jiggle the electrons and will *uniquely* lead to coherent scattering. Good candidates for applications are thus also quasielastic X-ray scattering and light scattering. In such techniques the Q -range tends to be small ($Q \approx 0$), but a lot of progress has been made in the last decade

³In diffraction studies static correlations lead to diffuse scattering. [8] It is perhaps tempting to invert this implication in the sense that absence of static correlations implies absence of diffuse scattering, but this is just wrong in dynamics.

⁴In this language of static and dynamical correlations, our statement that we do not consider environment-dependent dynamics, can be reformulated by saying that the jump times are not considered to depend on details in the static correlations between the orientations of the molecules inside or outside the dynamical cluster within a given configuration, but rather uniquely defined by the cog-wheel mechanism on this dynamical cluster.

in inelastic X-ray scattering techniques using synchrotron radiation, rendering available large Q -values combined with good energy resolution (≈ 1 meV). [9] When there is no energy information, the energy-integrated quasielastic scattering will still yield the \mathbf{Q} -dependence of the diffuse scattering.⁵

Extremely high resolutions can be obtained with the so-called speckle technique which allows one to study relaxation on a time scale of the order of 15 minutes! [10] Very good resolutions (neV) can also be obtained by nuclear resonance methods using synchrotron radiation [11] (e.g. exciting the 14.41 keV Mössbauer level of ^{57}Fe), but in general this is an incoherent process (as in this process the radiation interacts with the nuclei rather than with the electrons). Under certain experimental conditions the process is nonetheless coherent, but then the quasielastic scattering has to be detected against a very strong background of elastic scattering.

B. Scope of experimental phenomena

Coherent quasielastic neutron scattering studies are rare and this is certainly due to the difficulty of treating the problem theoretically. Incoherent quasielastic neutron scattering can often be modeled by a system of coupled rate equations, that one can solve analytically. But describing correlations, as probed by coherent quasielastic scattering, along such lines proves difficult. One solution to this problem is to drop the ideal of an analytical description all together and to make Monte Carlo [12] or molecular dynamics [13] simulations, but then fitting some variable parameters of the model to the experimental data will no longer be possible.

There are two main categories of stochastic motion that lead to (non-magnetic) quasielastic scattering, viz. translational diffusion and rotational relaxation.⁶ Our paper does not deal with translational diffusion.⁷ There exists a generalization of the Chudley-Elliott model that permits to calculate the coherent quasielastic neutron scattering signal for translational jump diffusion on a lattice. But this is an average description in that it is based on rate equations which rely on the assumption that the concentrations are rigorously homogeneous throughout the sample. [15] For the sake of completeness we refer the reader interested in theoretical aspects of translational diffusion to references [12] and [16]. The bulk of the experimental efforts have focused on the diffusion of D in NbD_x [17], Ag in silver halides [18] and in Ag_2Se [19], Rb in RbAg_4I_5 [20], Na in Na_3PO_4 [21] Oxygen in UO_2 [22] and F in fluorites [23].

⁵It may be noted that the formalism for inelastic X-ray scattering leads to expressions that link the scattering functions to the measured intensities in a way that looks identical to what we have for inelastic neutron scattering. However, important differences are very often passed under silence: The scattering functions that intervene in X-ray scattering are sums over all the *electrons* in the sample, while in neutron scattering they are sums over all *nuclei*. But both are generally noted as $S(\mathbf{Q}, \omega)$, without any explicit reference to this important distinction. Thus some work has to be done to render the two different definitions of scattering function comparable. It is not a priori given that the electrons will just move as the nuclei in the photon field. In Raman scattering e.g. the polarizability of the atom intervenes and gives rise to a coupling factor that can be hard to evaluate and is different from the simple expression $\mathbf{u} \cdot \mathbf{Q}$ that occurs for neutron scattering. (Here \mathbf{u} is the atomic displacement). The polarization of the electromagnetic radiation is important, etc... To our knowledge these points have never been worked out exhaustively for X-ray scattering.

⁶In molecular liquids both occur simultaneously and they can be coupled. [14]

⁷There is an unsurpassable intrinsic difference between rotational and translational diffusion. The point is easily made by considering the translational jump diffusion of two particles on a linear chain (of n positions). If the two particles could both occupy a same lattice site simultaneously then the configuration space would be just a square lattice (whose points $(1,1), (1,2), \dots, (i,j), \dots, (n,n)$, correspond to configurations where the first particle is located at the site with coordinate i , and the second particle at the site with coordinate j). As real particles cannot be in the same site at the same time, the diagonal of the square lattice ($i = j$) represents forbidden configurations. Once these points have been removed from the square lattice, we are left with two totally disconnected mirror-symmetric triangles (the mirror-symmetry corresponds to identical particle exchange). Eighter of these triangles can be taken as the configuration space for the two particles. The generalization to N particles leads to an N -dimensional simplex that is a $(1/N!)$ -th slice of an N -dimensional hypercube. The secular matrix that intervenes in the rate equations no longer has N -dimensional translational invariance in this truncated configuration space. The method of calculation we use in our paper is based on N -dimensional translational symmetry in configuration space and breaks thus down. (In models of correlated rotational jumps there are no such hyperplane cuts through configuration space corresponding to problems of excluded volume, but it is also a loss of global translational symmetry, splitting the configuration space in totally disconnected parts, that renders it impossible to perform the calculations for the non-ergodic case). If it were possible to overcome such fundamental difficulties one could make a mathematically rigorous calculation of the total scattering function for a hard-sphere liquid, by taking a continuum limit of an appropriate lattice gas model.

What kinds of rotational relaxation is our paper then able to address? Let us immediately state that our model may not have a perfect counterpart in the real world.⁸ It is a requirement of not breaking translational symmetry in configuration space that imposes the underlying assumptions of our paper. If these are not met, the calculation of the correlations is of a difficulty far beyond the methods we use.

We noted at the beginning of the Introduction that the rotating molecules do not need to have the symmetry of the rotational jump. This is important. If the symmetry of the molecules is the same as the symmetry of the jump, then the sample will look the same after the jump as before the jump. This means that the Fourier transform of the molecules can be factorized out in the calculations and we do not need to go through the more difficult approach of our paper.⁹

Combining these two limitations of feasibility and technical interest, the geometry of the nonadecane molecules is instrumental for visualizing the problem that we can treat, and for describing the (restricted) kind of correlations that we have in mind. The physical correlations between the nonadecane molecules that are really experimentally observed in the urea inclusion compound are of a different nature [27], which we are unable to treat (although this was not yet clear at the time we started this work). But this kind of correlations could exist in another system. The major lesson from our exercise must be that we give a non-trivial counter-example that indicates how coherent quasielastic neutron scattering may not always yield the information one expects on the basis of commonly accepted notions.

In our method the configuration space for the single-molecule dynamics is one-dimensional. It is however possible to generalize the formalism such as to recover also higher-dimensional single-molecule configuration spaces.¹⁰ This broadens the scope of possible applications further to three-dimensional rotations of molecules whose symmetry is not the same as that of the rotation symmetry. An example of such cases would be the rotational jumps of molecules of tetrahedral symmetry containing different isotopes (such that the symmetry is broken) as e.g. CH_3D , CD_3H , CH_2D_2 , NH_3D , $\text{C}^{79}\text{Br}_3^{81}\text{Br}$, $\text{C}^{79}\text{Br}_2^{81}\text{Br}_2$ [24], CBr_2Cl_2 [28], CBrCl_3 [28], etc... However in the physical world these molecules do not necessarily give rise to solids where our type of problems are encountered. In partially deuterated methane the physics is just different: Bulk CH_3D and CD_3H are either close to rotational diffusion, or there is quantum behaviour. In partially deuterated ammonia, the existence of exchange of D and H between the molecules complicates the picture.

Also octahedral molecules could be considered.¹¹ Finally, an important application of our result could be C_{60} . The (coherent) quasielastic neutron scattering signal of the rotational dynamics of this molecular crystal in its room temperature phase has been successfully described in terms of a model of completely independent rotors by Neumann *et al.* [29]. Although our results have been derived for rotational jumps rather than for continuous rotations as occur in C_{60} , they suggest by analogy that it cannot be claimed with certainty on the basis of the sole neutron data of Neumann *et al.* that the molecules would be totally independent.

IV. METHOD

The general method we use has been already described previously [1,5]. The idea is to formulate the problem in configuration space. The instantaneous configuration of the whole system is an abstract particle that diffuses on a network in this configuration space. The vertices of the network are the possible configurations of the system. (How to define them is illustrated by our example of the translational diffusion of two particles in footnote 7). When one single particle of the system makes a jump with a relaxation time τ , we say that the system “jumps” between two configurations with the relaxation time τ . Two configurations that are linked by such a move of one particle are connected by a line of the network carrying a label τ . The dynamics of our system is this way mapped isomorphically

⁸Eventually the assumptions that underly our model are dictated by the limits of our mathematical skills rather than the physics we attempted to address. As we will see, our approach of the problem leads to a description of the dynamics in terms of huge jump matrices. Analytical diagonalization of matrices of rank larger than 4 is in general not possible: As Galois has shown, beyond degree 4 there are no general solutions in terms of radicals for polynomial equations. A notable simplification can occur however, if we can make use of symmetry. It is mainly translational symmetry in configuration space that achieves the analytical diagonalization of the jump matrix in the present paper.

⁹Unless the dynamics is more complicated than a simple rotational jump model, due to supplementary problems such as translation-rotation coupling [24–26] etc...

¹⁰We will not give this derivation in order not to burden the paper. The proof runs as for the one-dimensional case *mutatis mutandis*.

¹¹A good example would be SF_6 , if it were not that the natural element fluorine is mono-isotopic (^{19}F), such that the simplification mentioned above can be applied. [25]

onto the problem of the diffusion of a single abstract particle (the system) on a network in configuration space. The only difference is that the embedding configuration space is of considerably higher dimension than physical space.

The physical problem can thus be described in terms of a set of coupled rate equations $\frac{d}{dt} \mathbf{P} = \frac{1}{\tau} \mathbf{M} \mathbf{P}$, where the column vector $\mathbf{P}(t)$ contains the probabilities $p_j(t)$ that the system is in configuration j at time t , τ is a relaxation time, and \mathbf{M} is the so-called jump matrix. The formal solution is worked out in reference [1] and does not contain further suprising steps or new ideas: By diagonalizing $\mathbf{M} = \mathbf{S} \mathbf{\Lambda} \mathbf{S}^{-1}$, we can write the solution of this set of coupled linear differential equations as $\mathbf{P}(t) = \mathbf{S} \exp(\mathbf{\Lambda} t / \tau) \mathbf{S}^{-1} \mathbf{P}(0)$. By plugging in the various initial conditions into $\mathbf{P}(0)$, we obtain then the full set of probabilities $p_{j,k}(t)$ that the system is in configuration j at time t if it was in configuration k at time 0. These are the quantities that are needed in the Van Hove correlation functions. A proper choice of initial conditions will also take into account the thermal occupation factors, i.e. entail the required thermal averaging. The total scattering function is obtained from the spatio-temporal Fourier transform of the thermal average of the correlation functions. In its final expression the total scattering function reads: $S(\mathbf{Q}, \omega) = \frac{1}{n^N} \mathbf{F} \mathbf{S} \mathcal{F}(e^{\mathbf{\Lambda} t / \tau}) \mathbf{S}^\dagger \mathbf{F}^\dagger$, where \mathbf{F} is the row matrix that contains the spatial Fourier transforms $F_{\mathbf{c}}$ of the configurations \mathbf{c} obtained by putting a Dirac measure of weight b_x at the position of each atom of type x (b_x is its coherent scattering length); \mathcal{F} stands for the temporal Fourier transform. The normalization factor $\frac{1}{n^N}$ is here written for the case of uncorrelated n -fold rotational jumps of N molecules.¹²

V. FORMULATION OF THE JUMP MATRIX

When there are no correlations between the molecules, the configuration space for the n -fold rotational jumps of N molecules on a lattice $\mathcal{L} \subset \mathbb{R}^d$ ($d \in \{1, 2, 3\}$), e.g. $\mathcal{L} = ([1, \ell] \cap \mathbb{N})^d$, $N = \ell^d$, will be a hypercubic lattice [30] $\mathcal{H} = (\mathbb{Z}/n)^N$ with cyclic boundary conditions in \mathbb{R}^N . (Each particle adds one dimension to configuration space: E.g. if there were just two molecules ($N = 2$) that make threefold rotational jumps ($n = 3$), the configuration space would be the square lattice of the $n^N = 3^2 = 9$ points $(1,1), (1,2), \dots, (i,j), \dots, (3,3)$. The configuration (i,j) corresponds then to the situation that particle 1 has orientation i and particle 2 orientation j . The boundary conditions are cyclic as each particle can go through the successive orientations $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$). For a three-dimensional sample ($d = 3$), the position vectors of the molecules will be $(j_x, j_y, j_z) \in \mathcal{L}$. The jump matrix \mathbf{M} is then defined by:

$$M_{\mathbf{c};\mathbf{d}} = -2N \delta_{\mathbf{c};\mathbf{d}} + \sum_{\mathbf{j} \in \mathcal{L}} (\delta_{\mathbf{c};\mathbf{d}+\mathbf{e}_{\mathbf{j}}} + \delta_{\mathbf{c};\mathbf{d}-\mathbf{e}_{\mathbf{j}}}). \quad (1)$$

The reader should not feel intimidated by the few very concise notations of this type that occur in the paper. They are mainly given for the sake of completeness. The main point he should capture is at which points in the jump matrix there are non-zero entries and how they look like. Eq. (1) is built up as follows. There is a unit vector $\mathbf{e}_{\mathbf{j}}$ in hypercubic space associated with each molecule (with position vector \mathbf{j}) that can turn: As we illustrated with the example of two particles above, each molecule adds a dimension to configuration space. When we start from a configuration \mathbf{c} and the molecule \mathbf{j} makes a rotational jump, the system goes to the configuration $\mathbf{d} = \mathbf{c} + \mathbf{e}_{\mathbf{j}}$. Hence, in the absence of correlations, a configuration $\mathbf{c} \in \mathcal{H}$ has $2N$ neighbours $\mathbf{d} = \mathbf{c} \pm \mathbf{e}_{\mathbf{j}}$, where $\mathbf{j} = (j_x, j_y, j_z) \in \mathcal{L}$: At the line corresponding to \mathbf{c} in the jump matrix there are thus non-zero entries at all columnar positions corresponding to the configurations $\mathbf{d} = \mathbf{c} + \mathbf{e}_{\mathbf{j}}$ and $\mathbf{d} = \mathbf{c} - \mathbf{e}_{\mathbf{j}}$, a fact which is expressed through the presence of the Kronecker delta's $\delta_{\mathbf{c};\mathbf{d}+\mathbf{e}_{\mathbf{j}}}$ and $\delta_{\mathbf{c};\mathbf{d}-\mathbf{e}_{\mathbf{j}}}$. The diagonal terms follow from these terms as in any other jump matrix for a diffusion problem.

¹²Generally speaking, treating the system in terms of configurations has several advantages. First of all, the total scattering function is invariant under the operation of identical-particle exchange, and this fact is automatically accounted for in our method, by considering as strictly identical all the configurations that can be obtained one from another by swapping identical particles. Consequently, identical particles are not tagged in our method: They remain undistinguishable. We do not loose time or efforts in enumerating tagged configurations. This reduces the number of configurations to be considered drastically: For each type of particles j , there can be a reduction by a factor $n_j!$, where n_j stands for the number of such identical particles of type j (provided that they can indeed be physically swapped by the dynamics). This is e.g. the reason why in the example of the translational diffusion of two particles in footnote 7, the configuration space can be taken as only one of the two triangles defined by the diagonal. (In the present case of rotational jumps, this simplification does not occur as the dynamics do not entail exchanges of molecules). The second advantage is that all static correlations that might occur inside a single configuration are automatically taken into account. In the calculation this transpires through the presence of the Fourier transform $\mathcal{F}_{\mathbf{c}}$ of the configuration \mathbf{c} . For this reason we further will never even mention these static correlations in the paper. The worth correlation only occurs in a dynamical sense.

The unit vectors $\mathbf{e}_{\mathbf{j}}$ are the generators of the hypercubic lattice \mathcal{H} , and each configuration \mathbf{c} accessible can be written as $\mathbf{c} = \sum_{\mathbf{j}} c_{\mathbf{j}} \mathbf{e}_{\mathbf{j}}$, with $c_{\mathbf{j}} \in \mathbb{Z}/n$. The hypercubic lattice \mathcal{H} represents all possible configurations that can be obtained by n -fold rotations, and therefore the configuration space when there are correlations will be a sublattice $\mathcal{S} \subset \mathcal{H}$ of \mathcal{H} .¹³

It is logical that we assume that due to the range of the intermolecular interactions, the set or cluster of jumping molecules extends to a neighbour shell of a certain order. Due to the translational invariance on the physical lattice \mathcal{L} , this cluster should be allowed to occur at every lattice site $\mathbf{j} \in \mathcal{L}$. A configuration \mathbf{c} will now be connected to other configurations $\mathbf{c} \pm \mathbf{v}_{\mathbf{j}}, \mathbf{j} \in \mathcal{L}$ on the sublattice \mathcal{S} , than $\mathbf{c} \pm \mathbf{e}_{\mathbf{j}}, \mathbf{j} \in \mathcal{L}$ as for the independent dynamics, and it is the set of ν relative position vectors $\mathbf{v}_{\mathbf{j}}$ that has to be defined. E.g. if on a two-dimensional square lattice $\mathcal{L} = ([1, \ell] \cap \mathbb{N})^2$ with cyclic boundary conditions, the jump of a molecule at (j_x, j_y) over $2\pi/n$ is always accompanied by opposite jumps over $-2\pi/n$ of its four first neighbours, then $\nu = \ell^2$ and

$$\mathbf{v}_{(j_x, j_y)} = \mathbf{e}_{(j_x, j_y)} - \mathbf{e}_{(j_x+1, j_y)} - \mathbf{e}_{(j_x-1, j_y)} - \mathbf{e}_{(j_x, j_y+1)} - \mathbf{e}_{(j_x, j_y-1)}, \forall (j_x, j_y) \in \mathcal{L}, \quad (2)$$

where the minus signs translate the fact that the rotations are opposite. We can understand this by decomposing the combined move mentally into a succession of single-molecule jumps: We first turn the molecule (j_x, j_y) , which changes the configuration from \mathbf{c} to $\mathbf{c} + \mathbf{e}_{(j_x, j_y)}$. Then we turn the molecule (j_x+1, j_y) , which changes the configuration further from $\mathbf{c} + \mathbf{e}_{(j_x, j_y)}$ to $\mathbf{c} + \mathbf{e}_{(j_x, j_y)} - \mathbf{e}_{(j_x+1, j_y)}$, etc... upto the final configuration $\mathbf{c} + \mathbf{v}_{(j_x, j_y)}$. The order in which we take these individual moves is not important, as in the combined move of the five molecules the system does not visit the intermediate configurations and goes immediately from the initial (\mathbf{c}) to the final configuration ($\mathbf{c} + \mathbf{v}_{(j_x, j_y)}$). On our network there will be a line that connects these two configurations and which will be labeled by τ . *Of course the relaxation time τ we use now has no longer any relationship whatsoever with the relaxation times we used in the problem of independent dynamics.* It is the relaxation time for a cluster, not for a molecule, and the probabilities we are dealing with here can in principle not be expressed as a product of probabilities as would occur if the rotors were independent.^{14,15} The $\nu = \ell^2$ vectors $\mathbf{v}_{\mathbf{j}}, \mathbf{j} = (1, 1), (1, 2), \dots, (\ell, \ell)$ are the generators of the sublattice \mathcal{S} . Using the hypercubic norm, we see that $\|\mathbf{v}_{(j_x, j_y)}\| = 5$.

As a second example, we could also imagine that each molecule at (j_x, j_y) has (for symmetry reasons) four equivalent alternatives to jump simultaneously with a single first neighbour. Then $\nu = 4\ell^2$ and $\forall (j_x, j_y) \in \mathcal{L}$:

$$\begin{aligned} \mathbf{v}_{(j_x, j_y), 1} &= \mathbf{e}_{(j_x, j_y)} - \mathbf{e}_{(j_x+1, j_y)}, \\ \mathbf{v}_{(j_x, j_y), 2} &= \mathbf{e}_{(j_x, j_y)} - \mathbf{e}_{(j_x-1, j_y)}, \\ \mathbf{v}_{(j_x, j_y), 3} &= \mathbf{e}_{(j_x, j_y)} - \mathbf{e}_{(j_x, j_y+1)}, \\ \mathbf{v}_{(j_x, j_y), 4} &= \mathbf{e}_{(j_x, j_y)} - \mathbf{e}_{(j_x, j_y-1)}. \end{aligned} \quad (3)$$

Here $\|\mathbf{v}_{(j_x, j_y), r}\| = 2$ ($r \in \{1, 2, 3, 4\}$). We see thus that in the general situation with correlations the jump matrix \mathbf{M} will be defined by

¹³We would like to stress that there is no underlying assumption related to representing the various configurations as points on a hypercubic lattice, for the mere convenience of enumerating them more easily. This also true when the rotors are not independent. More specifically, it does not imply any factorization of probabilities as we would have in the case of independent rotors. The probabilities will be given by the topological connectivity of the network or graph that links these points. These lines could be very different from the edges of the hypercubes of the hypercubic lattice that occur in the case of independent dynamics. The probability for a jump between two configurations is taken into account by connecting the points that represent them by a line labeled with its relaxation time. Only if these probabilities themselves were factorized would we have an underlying independence.

¹⁴It must be obvious that the occurrence of a cluster is probabilistic: The model of Eq. (2) is perhaps best seen as part of a larger model wherein e.g. a molecule has some probability to turn alone, some probability to turn as given by Eq. (2), and some probabilities to turn even within other types of clusters (see e.g. Eq. (13) below). One should thus not use the definition of Eq. (2) to “prove” that the whole lattice should turn simultaneously: when (j_x, j_y) turns, (j_x+1, j_y) turns; then since (j_x+1, j_y) turns, (j_x+2, j_y) must also turn, etc... That would be an absurd way of misinterpreting of our aims.

¹⁵We must emphasize that further on our approach will only work since we assume translational invariance in configuration space \mathcal{H} : the types of possible rotational jumps of a molecule (or a cluster of molecules) and their respective probabilities do not depend on the specific orientation of that molecule or any other actual detail of the prevailing configuration of the system. This would be quite reasonable for the case of alkane molecules evoked, but nevertheless this remark implies that we have not exhausted all possible meanings of the concept correlation. (We are not dealing in the present paper with the additional complication that the dynamics could also depend on the actual local environment of the molecules. Defining systems of the latter type in a self-consistent way is already difficult in its own right. We briefly touch upon it in the Appendix.)

$$M_{\mathbf{c};\mathbf{d}} = -2N\rho\delta_{\mathbf{c};\mathbf{d}} + \sum_{\mathbf{j} \in \mathcal{L}} \sum_{r=1}^{\rho} (\delta_{\mathbf{c};\mathbf{d}+\mathbf{v}_{\mathbf{j},r}} + \delta_{\mathbf{c};\mathbf{d}-\mathbf{v}_{\mathbf{j},r}}), \quad (4)$$

where $\rho = \nu/\ell^d$ is the number of different types r of clusters per lattice site that can turn (i.e. $\rho = 4$ in the example of Eq. (3)). The definition of Eq. (4) is analogous to the one in Eq. (1) with each vector $\mathbf{e}_{\mathbf{j}}$ replaced by ρ vectors $\mathbf{v}_{\mathbf{j},r}$. We can more generally assume that the various possibilities labeled by r lead to different time constants. Drawing in the time constants into \mathbf{M} the jump matrix becomes:

$$M_{\mathbf{c};\mathbf{d}} = \sum_{r=1}^{\rho} \frac{1}{\tau_r} (-2N\delta_{\mathbf{c};\mathbf{d}} + \sum_{\mathbf{j} \in \mathcal{L}} (\delta_{\mathbf{c};\mathbf{d}+\mathbf{v}_{\mathbf{j},r}} + \delta_{\mathbf{c};\mathbf{d}-\mathbf{v}_{\mathbf{j},r}})). \quad (5)$$

This notation can be further generalized by noticing that r corresponds to a difference (or translation) vector $\mathbf{t} \in \mathcal{L}$, $\sum_r \rightarrow \sum_{\mathbf{t} \in \mathcal{L}}$. We must then admit that for many values of \mathbf{t} , we will have $\frac{1}{\tau_{\mathbf{t}}} = 0$, or replace $\mathbf{t} \in \mathcal{L}$ by $\mathbf{t} \in \mathcal{G}$ where \mathcal{G} is a physical cluster:

$$M_{\mathbf{c};\mathbf{d}} = \sum_{\mathbf{t} \in \mathcal{G}} \frac{1}{\tau_{\mathbf{t}}} (-2N\delta_{\mathbf{c};\mathbf{d}} + \sum_{\mathbf{j} \in \mathcal{L}} (\delta_{\mathbf{c};\mathbf{d}+\mathbf{v}_{\mathbf{j},\mathbf{t}}} + \delta_{\mathbf{c};\mathbf{d}-\mathbf{v}_{\mathbf{j},\mathbf{t}}}). \quad (6)$$

We have just given some examples of possible correlations. In the present paper we will not further insist on writing down a general formalism that would cover all possible cases. First of all, there are too many possibilities. Secondly, we think that a general abstract formalism in configuration space [31] (which typically has a dimension $\approx 10^{24}$) with notations of the rather elaborate type that occur in Eq. (4-6), might easily conceal the rather simple ideas behind our method. We will therefore rather proceed by illustrating the method for examples of the type given, in order to familiarize us with its spirit.

VI. THE PROBLEM OF ERGODICITY

Since the hypercubic norms of the vectors $\mathbf{v}_{\mathbf{j}}$ are by definition larger than 1 in the presence of correlations, one would be inclined to think that \mathcal{S} will always be a *strict* subset of \mathcal{H} , which we expressed by saying that our dynamical problem is no longer “ergodic”. The real situation is more subtle. Taking the possibility of non-ergodicity seriously is a difficult task that we are unable to treat rigorously in general. In the Appendix we develop a physical argument to put forward the idea that we can relax the condition of ergodicity to a weaker criterium of *local* (as opposed to *global*) ergodicity. For the main stream of the paper we will henceforth assume ergodicity. But despite the fact that we devote here only a few lines to this assumption, we must stress that ergodicity is a vital issue for the validity of the calculations in the rest of the paper.

VII. SOLUTION OF THE JUMP MODEL IN THE ERGODIC CASE

When the system is ergodic, we can immediately use the eigenvectors we already established for \mathcal{H} in reference [1], and we will be able to derive without effort the eigenvalues from the form of $\mathbf{v}_{\mathbf{j},r}$, $\mathbf{j} \in \mathcal{L}$. Indeed, when the system is ergodic then the jump matrix in configuration space has translational symmetry along each of the directions defined by the N unit vectors $\mathbf{e}_{\mathbf{j}}$ that span \mathcal{H} . The eigenvectors are therefore just N -dimensional Bloch waves, i.e. $n^N \times 1$ column matrices $\mathbf{V}^{(\mathbf{k})}$ defined by $[\mathbf{V}^{(\mathbf{k})}]_{\mathbf{c}} = \exp[i\frac{2\pi}{n}(\mathbf{k} - \mathbf{k}_0) \cdot (\mathbf{c} - \mathbf{k}_0)]$, $\forall \mathbf{c} \in \mathcal{H}$. Here \mathbf{k}_0 stands for $(1, 1, 1, \dots, 1, 1) \in \mathbb{R}^N$ and is introduced to take into account the fact that the expression for the eigenvectors features the quantities k_{ξ} and c_{ξ} always under the form of linear combinations $(k_{\xi} - 1)$, and $(c_{\xi} - 1)$. The N -dimensional Bloch wave is obtained as a Kronecker product of N one-dimensional Bloch waves, just as a three-dimensional phonon can also be written as a Kronecker product of three one-dimensional Bloch-waves. (Each one-dimensional Bloch wave is a $n \times 1$ column matrix). Combining these eigenvectors with the definition of the $n^N \times n^N$ jump matrix \mathbf{M} in Eq. (4) yields the corresponding eigenvalues:

$$\lambda_{\mathbf{k}} = -2\rho N + 2 \sum_{\mathbf{j} \in \mathcal{L}} \sum_{r=1}^{\rho} \cos[\mathbf{v}_{\mathbf{j},r} \cdot (\mathbf{k} - \mathbf{k}_0)]. \quad (7)$$

This is exactly analogous to the way the eigenvalues of a phonon problem are obtained by operating the dynamical matrix on the Bloch wave eigenvectors. We just calculate $\mathbf{M}\mathbf{V}^{(\mathbf{k})}$ using the definitions of \mathbf{M} and $\mathbf{V}^{(\mathbf{k})}$ and check that

the result can be rewritten as $\lambda^{(\mathbf{k})} \mathbf{V}^{(\mathbf{k})}$ for some value $\lambda^{(\mathbf{k})}$. For the phonon case in text books, this calculation is usually only written for a general line of the column matrix that represents the eigen vector, with the possible effect that the argument might not be recognized as perfectly analogous to the one we are dealing with here. E.g. in the case of Eq. (2) we have $N = \ell^2$, $\rho = 1$, $\forall \mathbf{j} \in \mathcal{L} : \mathbf{k}_0 \cdot \mathbf{v}_{\mathbf{j}} = -3$, such that Eq. (7) is more explicitly seen to yield

$$\begin{aligned} \lambda_{\mathbf{k}} = & -2\ell^2 + 2 \cos \left[\frac{2\pi}{n} (k_{(1,1)} - k_{(1,2)} - k_{(1,\ell)} - k_{(2,1)} - k_{(\ell,1)} + 3) \right] \\ & + 2 \cos \left[\frac{2\pi}{n} (-k_{(1,1)} + k_{(1,2)} - k_{(1,3)} - k_{(2,2)} - k_{(\ell,2)} + 3) \right] \\ & \vdots \\ & + 2 \cos \left[\frac{2\pi}{n} (k_{(j_x, j_y)} - k_{(j_x+1, j_y)} - k_{(j_x-1, j_y)} - k_{(j_x, j_y+1)} - k_{(j_x, j_y-1)} + 3) \right] \\ & \vdots \\ & + 2 \cos \left[\frac{2\pi}{n} (-k_{(1,\ell)} - k_{(\ell-1,\ell)} - k_{(\ell,1)} - k_{(\ell,\ell-1)} + k_{(\ell,\ell)} + 3) \right], \end{aligned} \quad (8)$$

where $\mathbf{k} = (k_{(1,1)}, k_{(1,2)}, \dots, k_{(j_x, j_y)}, \dots, k_{(\ell, \ell)})$, and $k_{(j_x, j_y)} \in \mathbb{Z}/n$. There are thus n^{ℓ^2} \mathbf{k} -vectors in the case of Eq. (2). In fact, a general configuration \mathbf{c} has ℓ^2 vector components: $\mathbf{c} = (c_{(1,1)}, c_{(1,2)}, \dots, c_{(j_x, j_y)}, \dots, c_{(\ell, \ell)})$. The coordinates $c_{(j_x, j_y)}$ can take n values representing the n possible orientations of the molecule at $(j_x, j_y) \in \mathcal{L}$. There are thus in total n^{ℓ^2} configurations, and for each of them there is a probability. The jump matrix \mathbf{M} works on the space of these n^{ℓ^2} configurations. An eigenvector $\mathbf{V}^{(\mathbf{k})}$ is a vector with n^{ℓ^2} entries $[\mathbf{V}^{(\mathbf{k})}]_{\mathbf{c}}$, where \mathbf{c} runs through all possible configurations. We can thus depicture $\mathbf{V}^{(\mathbf{k})}$ as a function (the Bloch wave): $\mathbf{V}^{(\mathbf{k})} : \mathbf{c} \rightarrow [\mathbf{V}^{(\mathbf{k})}]_{\mathbf{c}}$. Let us operate \mathbf{M} on an eigenvector. The first non-zero off-diagonal entry in \mathbf{M} corresponds to the possibility that \mathbf{c} undergoes a transformation to $\mathbf{c} + \mathbf{v}_{(1,1)}$. That will transform the function from $\exp[i \frac{2\pi}{n} (\mathbf{k} - \mathbf{k}_0) \cdot (\mathbf{c} - \mathbf{k}_0)]$, $\forall \mathbf{c} \in \mathcal{H}$ to $\exp[i \frac{2\pi}{n} (\mathbf{k} - \mathbf{k}_0) \cdot (\mathbf{c} + \mathbf{v}_{(1,1)} - \mathbf{k}_0)]$, $\forall \mathbf{c} \in \mathcal{H}$, i.e. multiply it by $\exp[i \frac{2\pi}{n} (k_{(1,1)} - k_{(1,2)} - k_{(1,\ell)} - k_{(2,1)} - k_{(\ell,1)} + 3)]$. Continuing this way with the possible transformations towards $\mathbf{c} + \mathbf{v}_{(1,2)}, \dots, \mathbf{c} + \mathbf{v}_{(\ell, \ell)}$, including also the possible transformations towards $\mathbf{c} - \mathbf{v}_{(1,1)}, \mathbf{c} - \mathbf{v}_{(1,2)}, \dots, \mathbf{c} - \mathbf{v}_{(\ell, \ell)}$, and finally adding the diagonal term we obtain the result announced in Eq. (8).

The whole part of the calculation involving the determination of the structure factors remains the same as for the case without correlations. In fact this calculation (based on the evaluation of $\mathbf{G} = \mathbf{F} \mathbf{S}$) is entirely defined by the values of the eigenvectors (\mathbf{S}) and the Fourier transforms of the configurations (\mathbf{F}) and these are not changed in the ergodic case. This means that Eqs. (35) and (37) of reference [1] remain valid. Using the same notations as in that paper, the Lorentzian $L(\hbar \lambda_{\mathbf{k}} / \tau, \omega)$ will be associated with $|G_{\mathbf{k}}|^2$, where

$$\begin{aligned} G_{k_{(1,1)}; k_{(1,2)}; \dots k_{(j_x, j_y)}; \dots k_{(\ell, \ell)}} = & \frac{1}{n} \sum_{j_x=1}^{\ell} \sum_{j_y=1}^{\ell} \sum_{c_{(j_x, j_y)}=1}^n \mathcal{F}_{c_{(j_x, j_y)}} e^{i \frac{2\pi}{n} (c_{(j_x, j_y)} - 1) (k_{(j_x, j_y)} - 1)} e^{i \mathbf{Q} \cdot \mathbf{r}_{(j_x, j_y)}} \\ & \times \delta_{1 k_{(1,1)}} \delta_{1 k_{(1,2)}; 1} \dots \delta_{1 k_{(j_x, j_y-1)}} \delta_{1 k_{(j_x, j_y+1)}} \dots \delta_{1 k_{(\ell, \ell-1)}} \delta_{1 k_{(\ell, \ell)}}. \end{aligned} \quad (9)$$

Here $\mathcal{F}_{c_{(j_x, j_y)}}$ is the Fourier transform of the molecule (j_x, j_y) (with orientation $c_{(j_x, j_y)}$) if it were placed at the origin. (The real position vector of this molecule is $\mathbf{r}_{(j_x, j_y)}$). Consequently, the structure factor of the elastic term remains the same. The structure factors of the quasielastic terms remain also the same. Just the widths of the Lorentzians have to be re-examined. Due to the presence of the Kronecker symbols in Eq. (9) only Lorentzians for \mathbf{k} -values which have one single component $k_{(j_x, j_y)} \neq 1$ are contributing. In our example on the square lattice, these are the Lorentzians with

$$\lambda_{\mathbf{k}} = -2\ell^2 + 2(\ell^2 - 5) + 10 \cos \left[\frac{2\pi}{n} (k_{(j_x, j_y)} - 1) \right], \quad (10)$$

since in $\lambda_{\mathbf{k}}$ there are $\ell^2 - 5$ terms with a vanishing argument in the cosines and 5 terms where the argument of the cosines collapse to $\frac{2\pi}{n} (k_{(j_x, j_y)} - 1)$. We recover thus miraculously the same Lorentzians with a width parameter $-2 + 2 \cos \left[\frac{2\pi}{n} (k_{(j_x, j_y)} - 1) \right]$ as in the case without correlations, except for the detail that the relaxation time τ that occurs in the rate equations is being replaced in the final result by a five times faster relaxation time $\tau/5$, which does not happen in the case without correlations.¹⁶ *There is only a possible renormalization of the relaxation time to be*

¹⁶But since we are dealing with clusters of 5 molecules, we might originally have had the intuition to put a value 5 times

used in the description of the jump dynamics. Conclusion: It is absolutely impossible to appreciate from a signal due to coherent neutron scattering alone if there are correlations or otherwise! One can only hope that a comparison with incoherent data might still yield some clues. This result will be general if the cardinal number $\#\mathcal{H}$ of the set of possible configurations \mathcal{H} is not altered by the presence of correlations (case (1) in the terminology of the Introduction). In fact, the factor 5 in our example comes from the circumstance that our clusters contain five molecules, such that $\mathbf{v}_{(j_x, j_y)}$ will contain five terms. Due to this $\lambda_{\mathbf{k}}$ will contain five terms that contain $(k_{(j_x, j_y)} - 1)$, each time combined with other terms of the general type $\pm(k_{(j'_x, j'_y)} - 1)$, that vanish since $k_{(j'_x, j'_y)} = 1$. All other contributions to $\lambda_{\mathbf{k}}$ are devoid of terms in $k_{(j_x, j_y)}$.

We have not addressed the possibility illustrated by the example of Eq. (3), where we have more than one type of cluster. In principle this case is not different in nature from the one embodied by Eq. (2), since there we also have already $\nu > N$, such that Eq. (2) represents two equations rather than one. Provided we have ergodicity we can derive for this model from Eq. (4) with $N = \ell^2, \rho = 4, (\forall \mathbf{j} \in \mathcal{L}) (\forall r \in \{1, 2, 3, 4\}) (\mathbf{k}_0 \cdot \mathbf{v}_{\mathbf{j}, r} = 0)$:

$$\begin{aligned} \lambda_{\mathbf{k}} = & -8\ell^2 + 2 \cos \left[\frac{2\pi}{n} (k_{(1,1)} - k_{(1,2)}) \right] + 2 \cos \left[\frac{2\pi}{n} (k_{(1,1)} - k_{(1,\ell)}) \right] \\ & + 2 \cos \left[\frac{2\pi}{n} (k_{(1,1)} - k_{(2,1)}) \right] + 2 \cos \left[\frac{2\pi}{n} (k_{(1,1)} - k_{(\ell,1)}) \right] \\ & + 2 \cos \left[\frac{2\pi}{n} (k_{(1,2)} - k_{(1,1)}) \right] + 2 \cos \left[\frac{2\pi}{n} (k_{(1,2)} - k_{(1,3)}) \right] \\ & + 2 \cos \left[\frac{2\pi}{n} (k_{(1,2)} - k_{(2,2)}) \right] + 2 \cos \left[\frac{2\pi}{n} (k_{(1,2)} - k_{(\ell,2)}) \right] \\ & \vdots \\ & + 2 \cos \left[\frac{2\pi}{n} (k_{(j_x, j_y)} - k_{(j_x+1, j_y)}) \right] + 2 \cos \left[\frac{2\pi}{n} (k_{(j_x, j_y)} - k_{(j_x-1, j_y)}) \right] \\ & + 2 \cos \left[\frac{2\pi}{n} (k_{(j_x, j_y)} - k_{(j_x, j_y+1)}) \right] + 2 \cos \left[\frac{2\pi}{n} (k_{(j_x, j_y)} - k_{(j_x, j_y-1)}) \right] \\ & \vdots \\ & + 2 \cos \left[\frac{2\pi}{n} (k_{(\ell, \ell)} - k_{(1, \ell)}) \right] + 2 \cos \left[\frac{2\pi}{n} (k_{(\ell, \ell)} - k_{(\ell-1, \ell)}) \right] \\ & + 2 \cos \left[\frac{2\pi}{n} (k_{(\ell, \ell)} - k_{(\ell, 1)}) \right] + 2 \cos \left[\frac{2\pi}{n} (k_{(\ell, \ell)} - k_{(\ell, \ell-1)}) \right], \end{aligned} \quad (11)$$

Expressing the selection rule from Eq. (9) that only Lorentzians are contributing which correspond to a \mathbf{k} -value that contains a single component $k_{(j_x, j_y)} \neq 1$, we just retain the Lorentzians with

$$\lambda_{\mathbf{k}} = -8\ell^2 + 2(4\ell^2 - 8) + 16 \cos \left[\frac{2\pi}{n} (k_{(j_x, j_y)} - 1) \right], \quad (12)$$

such that the widths are now again $-2 + 2 \cos \left[\frac{2\pi}{n} (k_{(j_x, j_y)} - 1) \right]$, this time with a prefactor 8, since there are in total 16 different moves that involve a jump of molecule (j_x, j_y) .

We may note that we have already covered quite realistically looking possibilities. The task of taking into account correlations of this type on a whole lattice definitely seemed daunting before we embarked on our method. The most realistic case would probably involve a distribution of cluster sizes, whereby each cluster has its own characteristic relaxation time. E.g. on the square lattice we could instead of Eq. (2), have relaxation times and clusters $\forall (j_x, j_y) \in \mathcal{L}$:

$$\begin{aligned} \tau_1 : \mathbf{v}_{(j_x, j_y), 1} &= \mathbf{e}_{(j_x, j_y)} - \mathbf{e}_{(j_x+1, j_y)} - \mathbf{e}_{(j_x-1, j_y)} - \mathbf{e}_{(j_x, j_y+1)} - \mathbf{e}_{(j_x, j_y-1)}, \\ \tau_2 : \mathbf{v}_{(j_x, j_y), 2} &= \mathbf{e}_{(j_x, j_y)} - \mathbf{e}_{(j_x+1, j_y)} - \mathbf{e}_{(j_x-1, j_y)} - \mathbf{e}_{(j_x, j_y+1)} - \mathbf{e}_{(j_x, j_y-1)} + \mathbf{e}_{(j_x-1, j_y+1)} + \mathbf{e}_{(j_x+1, j_y-1)} \\ &+ \mathbf{e}_{(j_x+2, j_y)} + \mathbf{e}_{(j_x-1, j_y-1)} + \mathbf{e}_{(j_x-2, j_y)} + \mathbf{e}_{(j_x, j_y+2)} + \mathbf{e}_{(j_x, j_y-2)} + \mathbf{e}_{(j_x+1, j_y+1)}, \end{aligned}$$

slower than in the uncorrelated case into the rate equations. If we do not allow for this, then we would end up with a speed-up of the quasielastic signal in the presence of reorienting clusters, which is quite unphysical, as it should in principle be more difficult to move a set of molecules rather than a single molecule. This use of a factor 5 based on a handwaving argument can only be considered as a first approximation. We have no means to elucidate this relationship any further, since the jump time a single molecule would have had if its jumps had been independent is just not available to the experimentalist. There could be a change in the jump time parameter between the cases of correlated and uncorrelated jumps, but this cannot be learned from an inspection of coherent scattering data alone, since there is no change in the structure factors.

(13)

where in the additional cluster we have included now all members of the second-neighbour shell, assuming that their rotational jumps are in phase with those of the central molecule, i.e. in opposite phase with all the members of the first-neighbour shell. This leads to Lorentzians with a width parameter $\frac{1}{\tau_1} \lambda_{\mathbf{k}}^{(1)} + \frac{1}{\tau_2} \lambda_{\mathbf{k}}^{(2)}$, where $\lambda_{\mathbf{k}}^{(1)}$ is given by Eq. (8), while $\lambda_{\mathbf{k}}^{(2)} = -2\ell^2 + 2 \sum_{(j_x, j_y) \in \mathcal{L}} \cos \left[\frac{2\pi}{n} (k_{(j_x, j_y)} - k_{(j_x+1, j_y)} - k_{(j_x-1, j_y)} - k_{(j_x, j_y+1)} - k_{(j_x, j_y-1)} + k_{(j_x-1, j_y+1)} + k_{(j_x+1, j_y-1)} + k_{(j_x+2, j_y)} + k_{(j_x-1, j_y-1)} + k_{(j_x-2, j_y)} + k_{(j_x, j_y+2)} + k_{(j_x, j_y-2)} + k_{(j_x+1, j_y+1)} - 5) \right]$. We can appreciate that in general the width parameter for the Lorentzian $L_{\mathbf{k}}$ will be

$$\sum_{r=1}^{\rho} \frac{1}{\tau_r} (-2N + 2 \sum_{\mathbf{j} \in \mathcal{L}} \cos \left[\frac{2\pi}{n} \mathcal{P}_{\mathbf{j}, r} \right]), \quad (14)$$

since each cluster, i.e. each term $\mathbf{v}_{\mathbf{j}, r}$ introduces a term $-2N + 2 \sum_{\mathbf{j} \in \mathcal{L}} \cos(2\pi \mathcal{P}_{\mathbf{j}, r}/n)$, where the polynomial $\mathcal{P}_{\mathbf{j}, r}$ in the k 's is obtained by replacing each symbol \mathbf{e} by a symbol k in the definition of $\mathbf{v}_{\mathbf{j}, r}$ and adding $-\mathbf{k}_0 \cdot \mathbf{v}_{\mathbf{j}, r}$. After combining with $\delta_{1 k_{(1,1)}} \delta_{1 k_{(1,2)}} \dots \delta_{1 k_{(j_x, j_y-1)}} \delta_{1 k_{(j_x, j_y+1)}} \dots \delta_{1 k_{(\ell, \ell-1)}} \delta_{1 k_{(\ell, \ell)}}$ in the example of Eq. (13) we recover $-4(\frac{5}{\tau_1} + \frac{13}{\tau_2}) \sin^2 \left[\frac{\pi}{n} (k-1) \right]$ provided $\mathcal{S} = \mathcal{H}$. (Here we have used the fact that the set of values $k_{(j_x, j_y)} \in \mathbb{Z}/n$ is the same for all molecules (j_x, j_y) , such that identical values coming from different values of (j_x, j_y) can be regrouped in a term where the k -value is simply noted as k). The more different types of clusters one includes, the more likely the configuration space \mathcal{S} will cover the whole of \mathcal{H} . In fact, if also single-molecule jumps are allowed we forcedly end up with $\mathcal{S} = \mathcal{H}$. Also for the final expression of the Lorentzian widths after the application of the selection rules it is not difficult to derive the general result: $-4 \left[\sum_{r=1}^{\rho} (m_r/\tau_r) \right] \sin^2 \left[\frac{\pi}{n} (k-1) \right]$, where m_r is the number of molecules involved in cluster r . The use of the quantity m_r exploits the fact that in general the correlations between the molecules will be symmetrical. The most striking point is that all this follows almost effortlessly, even for very complex situations, as the translational invariance on \mathcal{H} establishes a kind of dictionary $\mathbf{v}_{\mathbf{j}, r} \rightarrow \mathcal{P}_{\mathbf{j}, r}$ which allows immediately to write down the eigenvalues, and that these eigenvalues are further tremendously simplified by the selection rule for the \mathbf{k} -values.

VIII. CONCLUSION

We conclude: Apart from a possible renormalization of the jump time, the signal in presence of correlations of the type we considered is the same as in total absence of correlations. In other words: Coherent quasielastic neutron scattering is unable to reveal possible correlations of the type we considered between the rotational jumps of the molecules. This is a clear, but non-trivial result. We may call it paradoxical that coherent scattering cannot reveal the type of correlations we considered, while incoherent scattering can. The finding that the widths are renormalized calls for caution in the interpretation of such widths in the results of an experiment. One would be inclined to interpret them as simple quantities corresponding to the relaxation of a single molecule, while their real meaning could be quite different. That is another important result of our work.

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APPENDIX: THE PROBLEM OF ERGODICITY

A. Why the problem is not simple

As the hypercubic norms of the vectors $\mathbf{v}_{\mathbf{j}}$ are by definition larger than 1 in the presence of correlations, one might believe that we never have ergodicity. They span a larger fundamental cell in hyperspace than the unit cell that occurs with independent dynamics, and therefore less of such cells should be contained in \mathcal{H} . But since we have cyclic boundary conditions in each dimension of the hypercubic lattice \mathcal{H} this is not necessarily true. A good example to illustrate this point is the transformation $\mathbf{v}_1 = \mathbf{e}_x + \mathbf{e}_y$, $\mathbf{v}_2 = \mathbf{e}_x - \mathbf{e}_y$ on a square lattice, which splits \mathbb{Z}^2 into two sublattices, one with integer and one with half-integer coordinates in the not normalized basis $\mathbf{v}_1, \mathbf{v}_2$. But if we apply this transformation to the restriction $(\mathbb{Z}/n)^2$, allowing for cyclic boundary conditions, then for n odd the vectors \mathbf{e}_1 and \mathbf{e}_2 will generate the whole lattice. We see thus that the problem of ergodicity we ran into is not as trivial to cope with as one might have thought at the start. It is however very important to know if we can claim that the problem is ergodic, since it determines if the calculation presented in this paper applies or otherwise.

Let us consider in the non-ergodic case a configuration \mathbf{c}_1 that occurs in \mathcal{H} , but not in the sublattice \mathcal{S} . On this configuration we can apply also the set of generators $\mathbf{v}_p, p = 1, 2, \dots, \nu$, to obtain the coset $\mathbf{c}_1 + \mathcal{S}$. The term coset is here appropriate since the lattices \mathcal{H} and \mathcal{S} can be considered as visualizations of a translation group. There might be a further configuration \mathbf{c}_2 that does not occur within $\mathcal{S} \cup (\mathbf{c}_1 + \mathcal{S})$. This way we construct $s = \#\mathcal{H}/\#\mathcal{S}$ disjoint cosets, based on initial configurations $\mathbf{c}_1, \mathbf{c}_2, \dots, \mathbf{c}_s$. Our lattice \mathcal{H} decomposes then as a Bravais lattice \mathcal{S} convoluted with a unit cell containing s “atoms” $\mathbf{c}_1, \mathbf{c}_2, \dots, \mathbf{c}_s$.

The correlated dynamics will then map onto the diffusion of an abstract particle (the configuration of the system) on the connected graph whose vertices are the points of \mathcal{S} . From any point of this graph it will be possible to wander to any other point of this graph. A point from another coset cannot be reached. Another coset represents thus a similar sample with similar dynamics, but the states of the sample represented by this coset cannot be reached starting from the states of the sample represented by \mathcal{S} . The s cosets represent thus s different samples with a similar structure and similar dynamics, that would be a kind of “enantiomorphs”. The different samples are characterized by the fact that they cannot have the same initial state. It is *a priori* not true that working with one of these s enantiomorphs should still yield the same \mathbf{Q} -dependence as for the independent dynamics. This is shown by the counter example with the Ising pseudospins given in the Introduction.

The main problem is that we would have to do the thermal averaging over \mathcal{S} rather than over \mathcal{H} . We would therefore need to determine how the lattice \mathcal{S} looks like and to find a set of basic vectors that generates it. In general, this will prove just too difficult a task, due to the huge dimensions of the configuration space. Furthermore, the averaging over \mathcal{S} will in general be too weak. Many sums in the averaging over \mathcal{H} reduce to Kronecker deltas (see reference [1]). In the average over \mathcal{S} , these sums will contain less terms, and therefore no longer necessarily yield results that are either 0 or 1.

B. Obvious mathematical criterium of non-ergodicity

One can think of one simple way to find out that the sample is not ergodic, viz. when the dynamics can be described by a single equation, as e.g. in the example of Eq. (2) and the dimension of \mathcal{S} is lower than the dimension of \mathcal{H} . There is a linear transformation with matrix \mathbf{T} :

$$[\mathbf{v}_{(1,1)}, \mathbf{v}_{(1,2)}, \dots, \mathbf{v}_{(2,1)}, \dots, \mathbf{v}_{(\ell,\ell)}]^\top = \mathbf{T}[\mathbf{e}_{(1,1)}, \mathbf{e}_{(1,2)}, \dots, \mathbf{e}_{(2,1)}, \dots, \mathbf{e}_{(\ell,\ell)}]^\top. \quad (15)$$

If $\det \mathbf{T} = 0$, it is clear that the dimension of \mathcal{S} is smaller than the dimension of \mathcal{H} . It is instrumental to note that $-(\mathbf{T} + 3\mathbf{I})$ is upto the factor $1/\tau$ equal to the jump matrix \mathbf{A} for the translational diffusion on the square lattice $\mathcal{L} = ([1, \ell] \cap \mathbb{N})^2$, which we know to diagonalize due to its translational symmetry when we assume cyclic boundary conditions. For other types of correlations than given by Eq. (2) an analogous argument will hold. The eigenvalues of \mathbf{A} are $-4 \sin^2 [\frac{\pi}{\ell} (k_x - 1)] - 4 \sin^2 [\frac{\pi}{\ell} (k_y - 1)]$, hence the eigenvalues of \mathbf{T} are $-3 + 4 \sin^2 [\frac{\pi}{\ell} (k_x - 1)] + 4 \sin^2 [\frac{\pi}{\ell} (k_y - 1)]$, such that:

$$\det \mathbf{T} = \prod_{k_x=1}^{\ell} \prod_{k_y=1}^{\ell} \{ -3 + 4 \sin^2 [\frac{\pi}{\ell} (k_x - 1)] + 4 \sin^2 [\frac{\pi}{\ell} (k_y - 1)] \}. \quad (16)$$

If one of the factors that occurs in this product is zero, we will know that the problem is non-ergodic. E.g. for $\ell = 12$ & $k_x = 3$ & $k_y = 4$, we have $-3 + 4 \sin^2 [\frac{\pi}{\ell} (k_x - 1)] + 4 \sin^2 [\frac{\pi}{\ell} (k_y - 1)] = 0$, such that in all cases where 12 is a factor of ℓ , the determinant will be zero, leading to a reduction of the dimensionality of the problem. We can infer from this that our dynamics very often will not be ergodic when we adopt cyclic boundary conditions on \mathcal{L} . We will therefore sketch a non-rigorous argument that suggests that for large samples non-ergodicity is not important.

C. A loophole of escape

Let us imagine that the neutron beam only illuminates a small part (\mathcal{L}) of the whole sample (\mathcal{L}'). We have then $\mathcal{L} \subset \mathcal{L}'$. We assume that the dynamics on \mathcal{L}' are not ergodic. Let us call \mathcal{H}' the configuration space that can be constructed from \mathcal{L}' and \mathcal{H}_1 the configuration space that could be constructed by independent dynamics from \mathcal{L} , if it were an isolated piece of sample. Let us drop from the description of the configurations in \mathcal{H}' everything that cannot be seen by the neutron beam, i.e. restrict their description to \mathcal{L} . Very often this incomplete, truncated description will generate all possible configurations of \mathcal{L} , i.e. the whole of \mathcal{H}_1 . In other words, the system is then not ergodic but the neutron beam cannot see it: \mathcal{L} has a (fake) apparent ergodicity. This boils down to a weakening of the ergodicity from a global to a local criterium. On any sizeable patch of the sample all possible configurations will then occur.

We will be in such a case of local ergodicity if we can build from a linear combination with integer coefficients of vectors $\mathbf{v}_{\mathbf{k}}$, a configuration $\mathbf{c}_{\mathbf{j}} \in \mathcal{H}'$, whose restriction to \mathcal{L} is equivalent to $\mathbf{e}_{\mathbf{j}}$, for some $\mathbf{j} \in \mathcal{L}$; put differently, if the projection of this configuration onto \mathcal{H}_1 is $\mathbf{e}_{\mathbf{j}}$. By translational invariance, we will then be able to do this $\forall \mathbf{j} \in \mathcal{L}$, and thus we will also be able to construct by linear combination any configuration $\mathbf{c} \in \mathcal{H}_1$, i.e. we can build a set whose projection is the whole of \mathcal{H} .

In the case of Eq. (2) it looks quite plausible that this would be possible: We start with $\mathbf{v}_{\mathbf{j}}$. By using $\mathbf{v}_{\mathbf{k}}$ contributions from the second-neighbour shell we can zero the coefficients of the $\mathbf{e}_{\mathbf{k}}$ corresponding to the first-neighbour shell, and so we can proceed further outwards shell after shell, upto arbitrary distances from \mathbf{j} . For the example of the dynamics given by Eq. (2) we have verified in detail that this works out. There are no conclusions to be drawn from this single case for any other possible model. One will have to check case per case if one can fall back onto such an argument of local ergodicity.

IX. APPENDIX 2. DEFINING ENVIRONMENT-DEPENDENT DYNAMICS

We want to show here how one can define environment-dependent dynamics self-consistently. This will allow us to explain why we are not able to treat such dynamics by our method. Let $\mathbf{c} \in \mathcal{H}$ be a configuration, $\mathbf{c} = \sum_{\mathbf{j} \in \mathcal{L}} c_{\mathbf{j}} \mathbf{e}_{\mathbf{j}}$. If we want to jump from \mathbf{c} to $\mathbf{c} \pm \mathbf{e}_{\mathbf{j}}$ we must look at the environment of the molecule at \mathbf{j} , i.e. we must look at the local configuration built by all the molecules that belong to a cluster $\mathbf{j} + \mathcal{G}$ centered around \mathbf{j} , where \mathcal{G} is a set of relative position vectors. The local configuration defined by these molecules is described by the coefficients $c_{\mathbf{j}+\mathbf{g}}, \mathbf{g} \in \mathcal{G}$, i.e. by $(c_{\mathbf{j}+\mathbf{g}_1}, c_{\mathbf{j}+\mathbf{g}_2}, \dots, c_{\mathbf{j}+\mathbf{g}_\ell}, \dots, c_{\mathbf{j}+\mathbf{g}_\mu}) \in (\mathbb{Z}/n)^\mu$, where μ is the number of molecules inside \mathcal{G} . To each such multiplet of n^μ vectors will correspond a relaxation time

$$\tau(c_{\mathbf{j}+\mathbf{g}_1}, c_{\mathbf{j}+\mathbf{g}_2}, \dots, c_{\mathbf{j}+\mathbf{g}_\ell}, \dots, c_{\mathbf{j}+\mathbf{g}_\mu}). \quad (17)$$

Note that the quantities $c_{\mathbf{j}+\mathbf{g}_\ell}$ are only a small subset of the coordinates of \mathbf{c} . Some of these relaxation times will be equal for symmetry reasons, but the notation remains generally valid. This definition holds at any site \mathbf{j} , due to the translational invariance on \mathcal{L} . The relaxation time Eq. (17) goes with jumps $\mathbf{c} \leftrightarrow \mathbf{c} \pm \mathbf{e}_{\mathbf{j}}$, i.e. it goes with $-2\delta_{\mathbf{c},\mathbf{d}} + \delta_{\mathbf{c},\mathbf{d}+\mathbf{e}_{\mathbf{j}}} + \delta_{\mathbf{c},\mathbf{d}-\mathbf{e}_{\mathbf{j}}}$, such that we have

$$M_{\mathbf{c},\mathbf{d}} = \sum_{\mathbf{j} \in \mathcal{L}} \frac{-2\delta_{\mathbf{c},\mathbf{d}} + \delta_{\mathbf{c},\mathbf{d}+\mathbf{e}_{\mathbf{j}}} + \delta_{\mathbf{c},\mathbf{d}-\mathbf{e}_{\mathbf{j}}}}{\tau(c_{\mathbf{j}+\mathbf{g}_1}, c_{\mathbf{j}+\mathbf{g}_2}, \dots, c_{\mathbf{j}+\mathbf{g}_\ell}, \dots, c_{\mathbf{j}+\mathbf{g}_\mu})}. \quad (18)$$

If we further would like to introduce the possibility that molecules turn simultaneously, we will end up with

$$M_{\mathbf{c},\mathbf{d}} = \sum_{\mathbf{j} \in \mathcal{L}} \sum_{r=1}^{\rho} \frac{-2\delta_{\mathbf{c},\mathbf{d}} + \delta_{\mathbf{c},\mathbf{d}+\mathbf{v}_{\mathbf{j},r}} + \delta_{\mathbf{c},\mathbf{d}-\mathbf{v}_{\mathbf{j},r}}}{\tau^{(r)}(c_{\mathbf{j}+\mathbf{g}_1}, c_{\mathbf{j}+\mathbf{g}_2}, \dots, c_{\mathbf{j}+\mathbf{g}_\ell}, \dots, c_{\mathbf{j}+\mathbf{g}_\mu})}. \quad (19)$$

We can appreciate from such equations that the translational invariance on \mathcal{H} is completely lost as the relaxation times depend on \mathbf{c} . Although (atmost) “only” ρn^μ of them have been introduced, it is not so that we could define a unit cell of ρn^μ sites on \mathcal{H} and define a “Bravais lattice” of $N/(\rho n^\mu)$ cells in analogy with the matrix diagonalization procedure for a phonon problem. Indeed, there is translational invariance on \mathcal{L} as all clusters $\mathbf{j} + \mathcal{G}$ are congruent, but this does not carry over to \mathcal{H} , e.g. $\mathbf{e}_{\mathbf{j}+\mathbf{s}} - \mathbf{e}_{\mathbf{j}} \neq \mathbf{e}_{\mathbf{j}+2\mathbf{s}} - \mathbf{e}_{\mathbf{j}+\mathbf{s}}$, although $(\mathbf{j} + \mathbf{s}) - \mathbf{j} = (\mathbf{j} + 2\mathbf{s}) - (\mathbf{j} + \mathbf{s})$.

The loss of translational symmetry has dramatic consequences. We can no longer diagonalize the jump matrix by simple arguments of translational symmetry and we run out of methods. There are other types of symmetry present, but these are not high enough to simplify the problem in any significant way. Therefore, in this case we cannot expect to recover a behaviour where the elastic intensity would vanish between the Bragg peaks, and the coherent quasielastic intensity would not reveal the correlations present.

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